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Percolation Effects on the Decay of Admolecules

by

D. L. Lin, X. Li, Zhen-Ya Li and Thomas F. George

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Percolation effects on the decay of admolecules

D. L. Lin, X. Li and Zhen-Ya Li*
Department of Physics and Astronomy
State University of new York at Buffalo
Buffalo, New York 14260

Thomas F. George
Departments of Chemistry and Physics
Washington State University
Pullman, Washington 99164-1046

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Abstract

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* On leave of absence from Suzhou University, Suzhou 215006, China.

I. Introduction

It is well known that in a two-component particle composite material, the conductivity exhibits singular behavior near a percolation threshold, namely, a composition at which one of the constituents forms a connected path extending throughout the material.[1] As an example, the effective conductivity of a composite material composed of metal and insulator particles varies as $(q-q_c)^{-t}$, near the metal percolation threshold q_c, where q is the volume fraction of the metal and t is a characteristic exponent which remains to be determined. Similar behavior has also been found for the nonlinear susceptibility in the static limit.[2]

In addition to static properties, optical properties of the two-component composite material, both linear and nonlinear, have been extensively studied.[3-9] In general, composite materials have optical properties very different from those of their constituents, especially in the vicinity of the percolation threshold. For instance, the observation of a large enhancement (10^6-10^8) of the effective optical nonlinearity has been reported[7] in composite materials. It is therefore interesting to investigate their optical properties near the percolation threshold.

On the other hand, optical properties of an atomic system located near a solid surface can change qualitatively depending upon the structure of the substrate. Detailed information about the spectroscopic properties of the adspecies can be employed to probe the electronic and optical properties of the substrate. A recent study of the decay rate and resonance fluorescence spectrum of a molecule adsorbed near the surface of a particle composite[10] illustrates clearly the strong dependence of the energy transfer on the volume fraction of the impurity.

We investigate in this communication the effect of percolation on the energy transfer between an admolecule and the substrate. We consider a two-component granular material, that is, a random mixture of two kinds of small particles: one is an insulator not absorptive to the light, and the other is a metal. Optical properties of this material are described by an effective dielectric function derived by means of the effective medium theory (EMT).[1,11-13] When one component of the composite just forms an infinite connected path through the material, it is at the percolation threshold. Thus, the conductivity increases suddenly when the metal granules just reach the percolation threshold. Our purpose is to investigate the luminescence decay rate of an admolecule near the surface of the composite which is in the vicinity of its percolation threshold. It is found that the decay rate shows a peak centered around the conduction percolation threshold at low frequencies, or when $\omega \ll \omega_p$. where ω_p is the plasmon frequency of the metal. For admolecules of high transition frequency, or $\omega \sim \omega_p$, the peak occurs at a higher q, indicating the possible existence of another percolation threshold. Implications of this and other results will be discussed.

II. Theory

We consider a molecule adsorbed at a distance d from the surface of a two-component particle composite material as the substrate. For simplicity, we assume that the molecule has only two levels $|+$ and $|->$ with an energy difference $E_+ - E_- = \hbar\omega$.

The optical spectrum of the scattered field from an admolecule can in general be treated by means of a set of surface-dressed optical Bloch equations[14] including effects of the surface-reflected field. For the present purpose of the luminescence decay-rate study, it is sufficient to consider the

admolecule as a damped harmonic oscillator. Thus, the Hamiltonian of the system is given by

$$H = (\omega - i\gamma_o)a^\dagger a - p^* a^\dagger E_R \quad , \tag{1}$$

where $a^\dagger(a)$ is the creation (annihilation) operator for the molecular dipole oscillator whose matrix element is denoted by p, and E_R denotes the reflected electric field in the direction of the dipole moment. Following Dekker's quantization procedure for dissipative systems,[15] the equation of motion for the density operator of the molecular system can be written as

$$\dot{\rho} = -\frac{i}{\hbar}[a^\dagger, [a, H]\rho] + \frac{i}{\hbar}[\rho[H^\dagger, a^\dagger], a] \quad . \tag{2}$$

With the help of Eqs. (1) and (2), we find that the mean value of the operator obeys the equation

$$\frac{d}{dt}\langle a\rangle = Tr\langle \rho \dot{a}\rangle = -i(\omega+\Delta\omega)\langle a\rangle - \gamma\langle a\rangle \quad , \tag{3}$$

with the decay rate given by

$$\gamma = \gamma_o\left[1 + \frac{3}{2\sqrt{\epsilon_1}\kappa_0^3} Im(E_R/\mu_0)\right] \quad . \tag{4}$$

In the above derivation, we have made use of the following definitions. Both the frequency shift $\Delta\omega$ and width change $\Delta\gamma = \gamma - \gamma_0$ are caused by the presence of the surface. The decay rate of the excited molecule inside a homogeneous medium is $\gamma_0 = \frac{2}{3}\sqrt{\epsilon}_1|p|^2\omega^3/c^3$, and the dipole moment operator is $\mu_0 = pa$. In

addition, we have assumed that the molecule is in a medium of dielectric constant ϵ_1, and $\kappa_0 = \omega/c$.

As is well known,[10,14] the reflected field E_R for an emitting dipole with moment μ_0 located near the surface of a solid substrate can be found by solving Maxwell equations with corresponding boundary conditions. Since the substrate we are considering now is a two-component particle composite material with symmetric microgeometry, E_R must depend on the optical properties of both components as well as their volume fractions. Therefore measurements of the decay rate alone can reveal much of the characteristic properties of the substrate via E_R. Here we just consider the case in which the admolecule is oriented such that its dipole moment is normal to the substrate surface. The decay rate can then be worked out from Eq. (4) by the standard procedure,[10] namely,

$$\gamma = 1 - \frac{3}{2} Re\int_0^\infty \frac{\kappa^3 dk}{\mu_1} \frac{\epsilon_1\mu_2 - \epsilon_2\mu_1}{\epsilon_1\mu_2 + \epsilon_2\mu_1} \exp(2i\mu_1 x) \quad , \tag{5}$$

where ϵ_2 is the effective dielectric function of the substrate, $\mu_1 = \sqrt{1-\kappa^2}$, $\mu_2 = \sqrt{\epsilon_2/\epsilon_1 - \kappa^2}$ and $x = \sqrt{\epsilon_1}\omega d/c$. The rate in Eq. (5) is measured in the unit of γ_0.

For a symmetric conductor-insulator particle composite, the conductivity or optical susceptibility is usually treated by the extended EMT.[16] The effective dielectric function $\epsilon_2(\omega)$ is given in this theory by

$$\frac{\epsilon_2 - \epsilon_b}{\epsilon_b + (\frac{1}{q_c} - 1)\epsilon_2} q + (1-q) \frac{\epsilon_2 - \epsilon_a}{\epsilon_a + (\frac{1}{q_c} - 1)\epsilon_2} = 0 \quad , \tag{6}$$

where $\epsilon_a(\epsilon_b)$ stands for the dielectric function of the insulator (metal), q is the volume fraction of the conductor in the composite, and q_c is the critical volume fraction of percolation for the connection of metal particles.[1] In the standard EMT, $q_c = 1/3$.

Equation (6) can be rewritten as

$$(\frac{1}{q_c} - 1)\epsilon_2^2 - \frac{1}{q_c}[(1-q-q_c)\epsilon_a + (q-q_c)\epsilon_b]\epsilon_2 - \epsilon_a\epsilon_b = 0 \quad . \tag{7}$$

The quadratic equation (7) has in general two solutions that are complex conjugate to each other. We are interested in a physical solution $\epsilon_2(\omega)$ which is a continuous function of ω and has a positive imaginary part. Since the percolation threshold of a metal-insulator composite material changes with the microgeometry structure of particles, q_c may be regarded as a parameter characterizing the microstructure of the two components.

III. Results and discussion

In our numerical analysis, we assume for definiteness a nonabsorbing insulator such as $A\ell_2O_3$ with real dielectric constant $\epsilon_a = 3$, while the dielectric function ϵ_b of the metal is given by

$$\epsilon_b = 1 - \omega_p^2/\omega(\omega+i\Gamma_p) \quad , \tag{8}$$

where Γ_p denotes the damping rate of the plasmon oscillation. For a typical metal such as silver, we take $\Gamma_p = 0.01\ \omega_p$. Other parameters we have to specify are the dielectric constant $\epsilon_1 = 1.5$ for fatty acid and $x = 0.2$, a

typical value which can always be satisfied by adjusting the molecular distance from the surface for a given transition frequency ω.

We first solve Eq. (7) for the effective dielectric function ϵ_2 of the composite substrate with given q_c and ω. Plotted as functions of the volume fraction q, both the real and imaginary parts of ϵ_2 are shown in Fig. 1 for $q_c = 0.3$ and three typical frequencies: (a) $\omega = 0.1\ \omega_p$ in the low-frequency region: The absorption part peaks around $q = q_c$, where the dispersion part changes its sign. Hence the substrate is metal-like for $q > q_c$ in low-frequency regime. Our numerical study shows similar results for different values of q_c; (b) $\omega = 0.35\ \omega_p$: Both the peak of the imaginary part and the zero of the real part move toward larger q; and (c) $\omega = \omega_p$: The real part remains positive in the whole range, and the imaginary part has a small peak around $q = 0.7$. We believe that this is due to the bulk effect on the percolation threshold, which we shall discuss later.

Since the surface plasmon contribution leads to a minimum in the denominator in Eq. (7),[17] this resonance condition determines the dispersion relation of the surface plasmon. If the substrate is nonabsorptive, the surface plasmons have infinite lifetime and $\epsilon_1\mu_2 + \epsilon_2\mu_1 = 0$. Because of the nonzero Γ_p in the present case, the lifetime remains finite. In the low-frequency region, say, $\omega/\omega_p \lesssim 0.2$, the absorption part of the optical susceptibility of the composite material is usually very large, as seen in Fig. 1(a), and hence the damping rate is too large for surface plasmons to propagate. In the high-frequency region, $\omega/\omega_p \gtrsim 0.9$, it is seen from Fig. 1(c) that the real part of ϵ_2 is always positive even though the imaginary part is much smaller. There can not be surface plasmon waves here either, because the real part of ϵ_2 must be negative (at least) for surface modes to exist.[18]

The decay rate is computed from (5) with $\epsilon_2(\omega)$ given by (7). Since we are interested in percolation effects on the energy transfer from the admolecule to the surface, γ is calculated as a function of the volume fraction q of the metal particles and is expressed in the unit of γ_0. It is well known that the conduction percolation threshold q_c depends sensitively upon the microstructure of the two-component system. For a metal-insulator system of symmetric microgeometry, q_c is not expected to exceed 0.5 normally. Some of our results are shown in Fig. 2, in which we have chosen the frequency ratio ω/ω_p such that there are almost no surface plasmons propagating on the substrate surface. Curves 1 and 2 in both cases (a) and (b) correspond to low frequencies ($\omega = 0.1\ \omega_p$) and high frequencies ($\omega = \omega_p$), respectively. Since surface plasmon waves are absent in these cases, the enhancement of the decay rate in every case shown in the figures must be due to absorption by metallic granules. We attempt below to understand qualitatively the peaks in these curves.

In the low-frequency regime, the absorption peak appears at around the conduction percolation threshold q_c of metallic granules, qualitatively in agreement with what has been found in Ref. 3 in which a simple model of $q_c = 1/3$ is assumed. This is understandable because only at $q \sim q_c$ there is sufficient metal component to absorb the energy transferred from the excited admolecule. As q increases further, metallic particles become closer to a bulk metal and the absorption rate is reduced again. This is because the collisions of carriers responsible for the absorption are usually more frequent in metallic particles than in the bulk. In the high-frequency regime, the position of the absorption peak can be very different for different q_c. When $q_c = 0.3$, curve 2 peaks at about $q = 0.7$ in Fig. 1(a), and when $q_c = 0.5$, it peaks at q_c in Fig. 1(b). To account for this interesting

phenomenon, we believe that in the optical wavelength range there exist two distinct percolation thresholds, where one results from the usual percolation formed by one connected path extending throughout the material and the other from the "surface percolation" formed by so many connected paths that almost the whole cross section is conducting.[19] For low frequencies, the usual percolation dominates and the optical behavior of the composite material is similar to that of the static case.[2,20] For high frequencies, the bulk of the metallic part in the granular material is responsible for the optical absorption in the substrate. Hence the peak of curve 2 clearly indicates the existence of a new percolation threshold resulting from the bulk effects.

When the transition frequency is such that there exist surface plasmon waves in the substrate, energy can be transferred from the excited admolecule both by the absorption processes described above and the excitation of surface plasmon waves. The latter is found much more important than the former. Numerical results are plotted in Fig. 3 for some typical cases. It is clearly seen that the decay rate is greatly enhanced, especially when $q \sim 0.75$ for $q_c = 0.3$ and when $q \sim 0.85$ for $q_c = 0.5$. A physical understanding of this behavior, however, is not straightforward, and further investigation is required.

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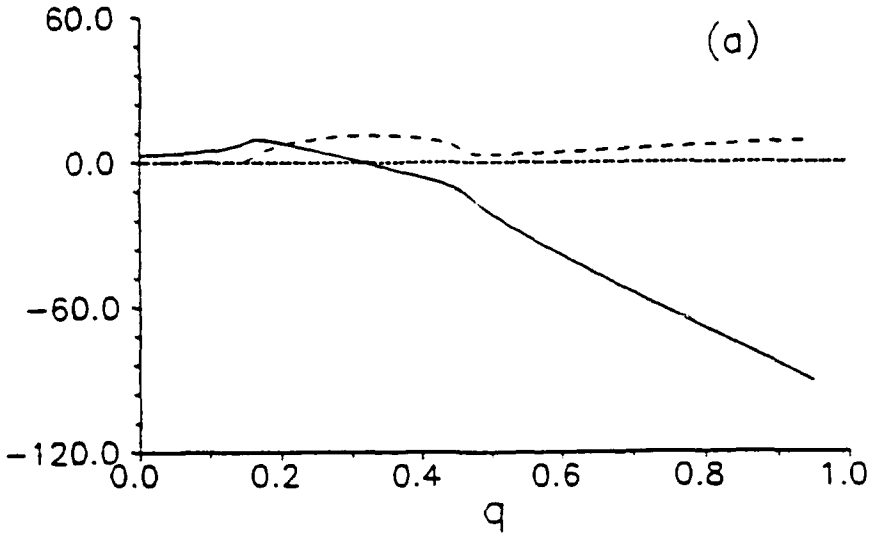
Figure Captions

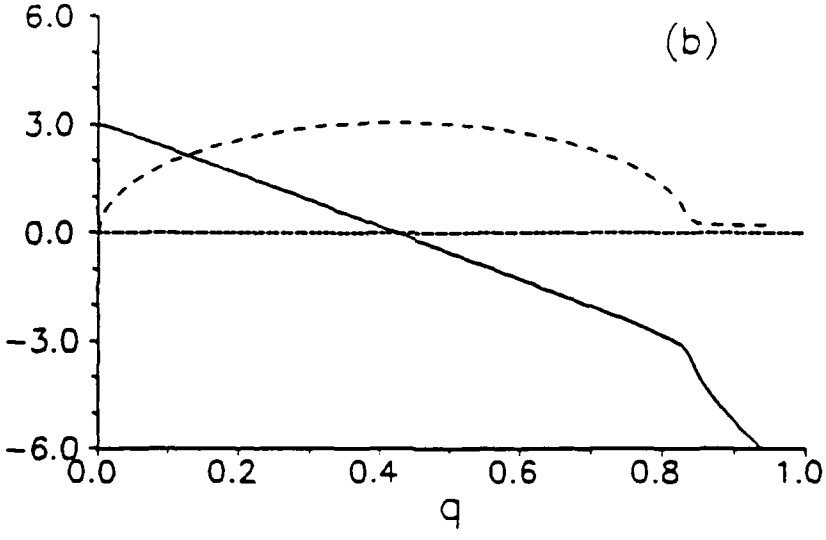
1. Effective dielectric function $\epsilon_2(\omega)$ vs volume fraction of metallic particles for $q_c = 0.3$. The solid (dashed) lines represent the real (imaginary) part of $\epsilon_2(\omega)$. (a) $\omega/\omega_p = 0.1$, (b) $\omega/\omega_p = 0.35$ and (c) $\omega/\omega_p = 1.0$

2. Luminescence decay rate γ of the admolecule as a function of q. Curve 1 is for $\omega/\omega_p = 0.1$ and curve 2 is for $\omega/\omega_p = 1.0$. (a) $q = 0.3$ and (b) $q = 0.5$.

3. Luminescence decay rate γ of the admolecule vs. q in the frequency region where the energy transfer from the admolecule to surface plasmons occurs. Curve 1: $q_c = 0.3$, $\omega/\omega_p = 0.35$; Curve 2: $q_c = 0.5$, $\omega/\omega_p = 0.45$.

Fig. 1


60.0
0.0
-60.0
-120.0
0.0
0.2
0.4
0.6
0.8
1.0
q
(a)


6.0
3.0
0.0
-3.0
-6.0
0.0
0.2
0.4
0.6
0.8
1.0
q
(b)

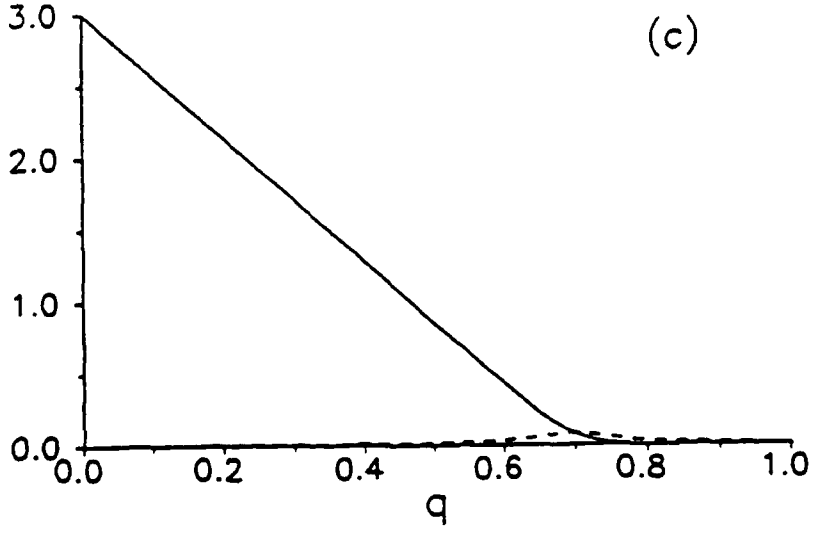

3.0
2.0
1.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
q
(c)

Fig. 2

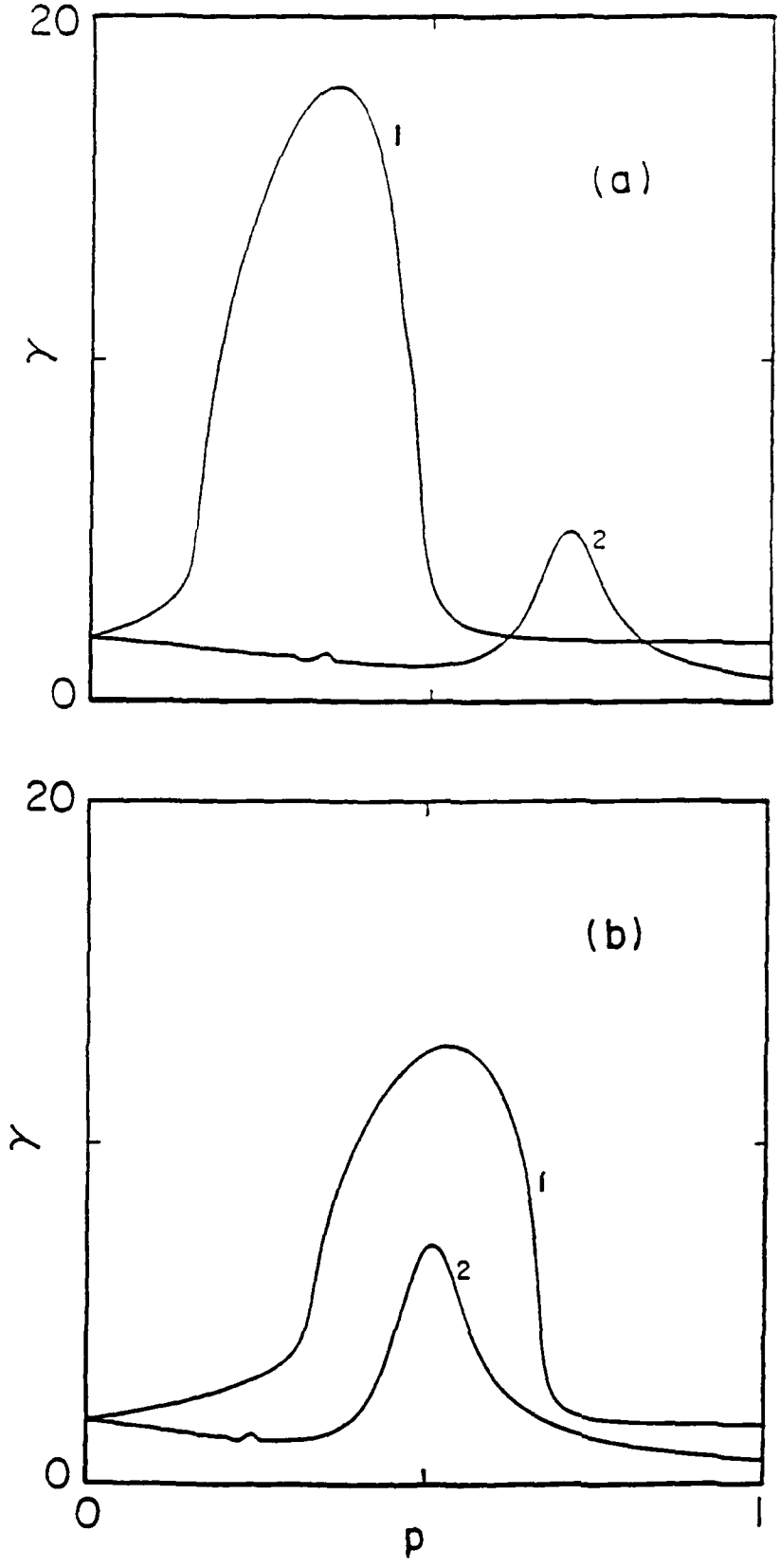
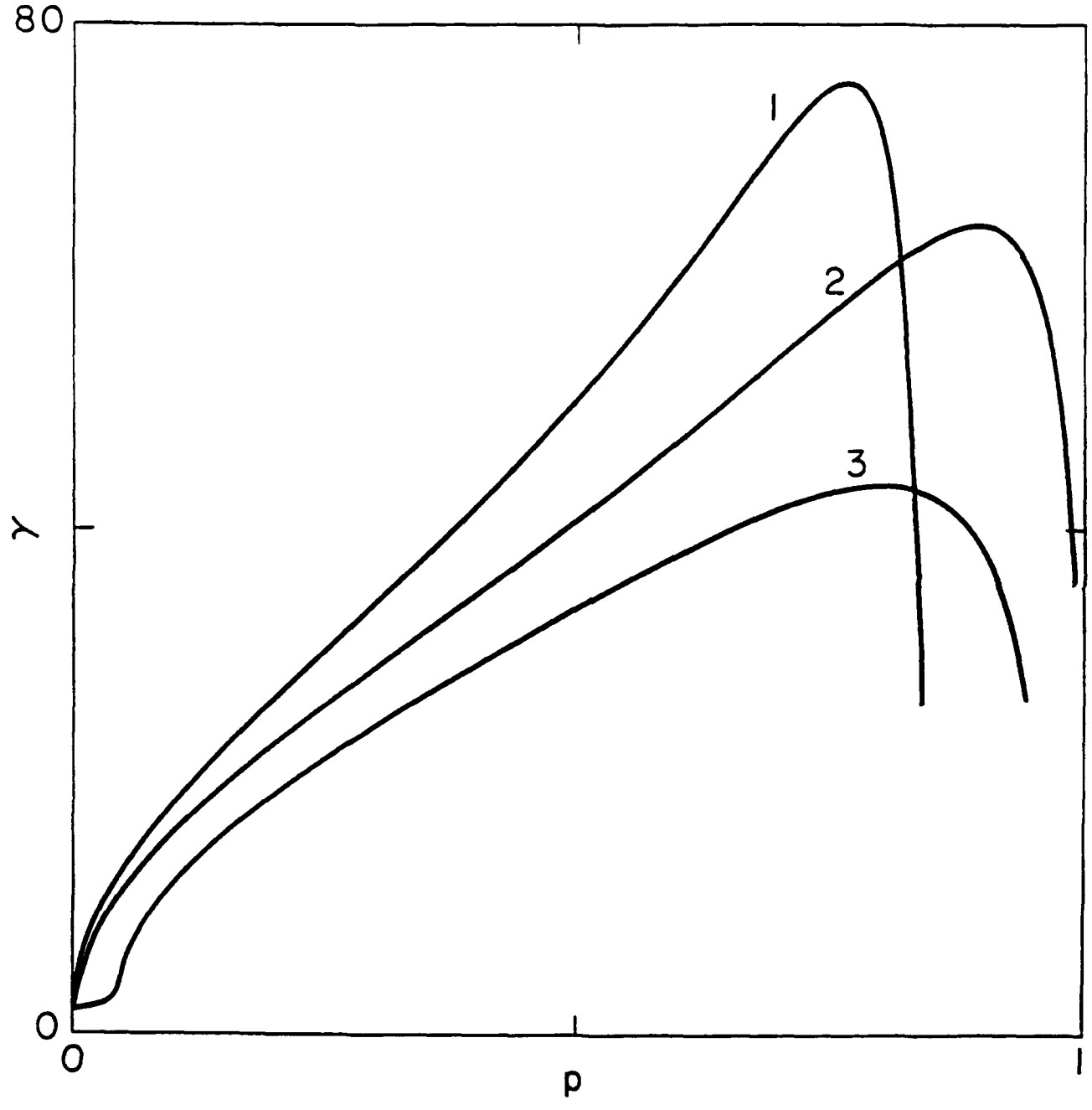



Fig. 3